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Tsoureas, Nikolaos, Maron, Laurent, Kilpatrick, Alexander F R, Layfield, Richard A and Cloke, F Geoffrey N (2020) Ethene activation and catalytic hydrogenation by a low-valent uranium pentalene complex. *Journal of the American Chemical Society*, 142 (1). pp. 89-92. ISSN 0002-7863

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Ethene Activation and Catalytic Hydrogenation by a Low-Valent Uranium Pentalene Complex

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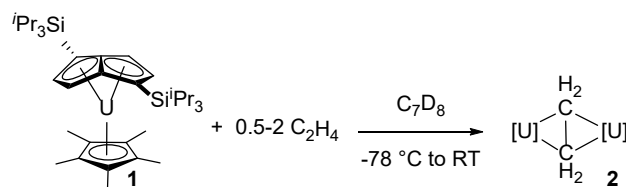
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ABSTRACT: The reaction of the uranium(III) complex $[\text{U}(\eta^8\text{-Pn}^{++})(\eta^5\text{-Cp}^*)]$ (**1**) ($\text{Pn}^{++} = \text{C}_8\text{H}_4(1,4\text{-Si}^i\text{Pr}_3)_2$, $\text{Cp}^* = \text{C}_5\text{Me}_5$) with ethene at atmospheric pressure produces the ethene-bridged di-uranium complex $[\{(\eta^8\text{-Pn}^{++})(\eta^5\text{-Cp}^*)\}_2\text{U}(\mu\text{:}\eta^2\text{:}\eta^2\text{-C}_2\text{H}_4)]$ (**2**). A computational analysis of **2** reveals that coordination of ethene to uranium reduces the carbon-carbon bond order from two to a value consistent with a single bond, with a concomitant change in the formal uranium oxidation state from +3 in **1** to +4 in **2**. Furthermore, the uranium-ethene bonding in **2** is of the δ -type, with the dominant uranium contribution being from f/d hybrid orbitals. Complex **2** reacts with hydrogen to produce ethane and re-form **1**, leading to the discovery that complex **1** also catalyzes the hydrogenation of ethene under ambient conditions.

Since the landmark synthesis of Zeise's salt,^{1–3} alkene complexes of transition metals have become a cornerstone of organometallic chemistry, forming the basis of many important catalytic reactions such as polymerization,⁴ hydrogenation,⁵ isomerization⁶ and hydroformylation.⁷ Whilst transition metal alkene complexes are common, such complexes of f -elements are extremely rare. Indeed, only two lanthanide-ethene complexes have been structurally characterised, the ethene-bridged dimers $[\{(\text{calix-pyrrole})\text{Ln}\}(\mu\text{:}\eta^2\text{:}\eta^2\text{-C}_2\text{H}_4)]$ with $\text{Ln} = \text{Nd}$ or Sm along with the structurally related pseudo-lanthanide complex $[\{\text{Sc}(\eta\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3})_2(\mu\text{:}\eta^2\text{:}\eta^2\text{-C}_2\text{H}_4)]$.^{8,9} In the actinide series, stable alkene complexes are unknown, although evidence of η^2 -alkene coordination to thorium and uranium has been provided by gas-phase and matrix isolation experiments.¹⁰ Furthermore, evidence for the ability of thorium and uranium to activate and transform alkenes has been reported,¹¹ and polymerization catalysts based on these lighter actinides are well known.^{12–14}

In light of these findings and the paucity of detailed understanding of actinide alkene complexes, we decided to pursue the synthesis and isolation of an η^2 -ethene complex of uranium. Since the reducing power of the uranium(III) sandwich complex $[\text{U}(\eta^8\text{-Pn}^{++})(\eta^5\text{-Cp}^*)]$ (**1**) ($\text{Pn}^{++} = \text{C}_8\text{H}_4(1,4\text{-Si}^i\text{Pr}_3)_2$, $\text{Cp}^* = \text{C}_5\text{Me}_5$) allows the formation of a stable uranium-dinitrogen complex¹⁵ and the activation of *tert*-butylphosphalkyne,¹⁶ this complex was identified as potentially being suitable for ethene activation. Thus, addition of 0.5–2 equivalents of C_2H_4 *via* a Töpler pump to an olive-brown solution of **1** in C_7D_8 produced an immediate colour change to a deep brown (Scheme 1).



Scheme 1. Reaction of **1** with ethene to give **2**. $[\text{U}] = [\text{U}(\eta^8\text{-Pn}^{++})(\eta^5\text{-Cp}^*)]$.

¹H-NMR spectroscopy revealed the formation of a new major species in solution (>90%, also see below), consistent with the formation of a C_2 symmetric molecule. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of this reaction mixture shows that the resonance at $\delta(^{29}\text{Si}) = -174.0$ ppm due to **1** has disappeared and two new signals appear at -107.0 and -199.4 ppm. These spectroscopic features are reminiscent of those observed for the dinitrogen-bridged di-uranium complex $[\{(\eta^8\text{-Pn}^{++})(\eta^5\text{-Cp}^*)\}_2\text{U}(\mu\text{:}\eta^2\text{:}\eta^2\text{-N}_2)]$ and, as such, we envisaged that the di-uranium complex $[\{(\eta^8\text{-Pn}^{++})(\eta^5\text{-Cp}^*)\}_2\text{U}(\mu\text{:}\eta^2\text{:}\eta^2\text{-C}_2\text{H}_4)]$ complex **2**, featuring a $\mu\text{:}\eta^2\text{:}\eta^2$ -ethene ligand, had formed. This was further confirmed by the synthesis of the carbon-13 isotopomer of **2** (**2**- ^{13}C), using 99%-enriched $^{13}\text{C}_2\text{H}_4$, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of which features a resonance for coordinated ethene as a singlet at -54.0 ppm. The proton-coupled ^{13}C NMR spectrum appears as a complicated multiplet, characteristic of a second-order spectrum due to the magnetic inequivalence of the protons. Nevertheless, a $^1J_{\text{CH}}$ coupling constant of *ca* 125 Hz can be extracted, which is characteristic of an aliphatic C–H bond.¹⁷

Complex **2** crystallizes readily from toluene, thus allowing unambiguous confirmation of its molecular structure (Figure 1). It was not necessary to crystallize **2** under an atmosphere of C_2H_4 and the ethene ligand is not labile in the solid state even under vacuum. This molecular structure was corroborated by the $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ solid-state NMR spectra of **2**- ^{13}C , which agree well with the corresponding solution NMR spectra discussed above, *i.e.* the ethene resonance occurs at $\delta = -59.92$ ppm in the $^{13}\text{C}\{^1\text{H}\}$ spectrum, and the silyl substituents occur at $\delta = -109.8$ and -216.1 ppm in the ^{29}Si NMR spectrum, which confirms that the solid-state structure is retained in solution.

As shown in Figure 1, the C_2H_4 ligand coordinates to two uranium centers and the approximate C_2 molecular symmetry is consistent with the NMR spectra. The C1–C2 bond distance of the C_2H_4 ligand in **2** has lengthened significantly to 1.496(7) Å relative to that of 1.332(2) Å in free ethene¹⁸ and approaches a value typical of a carbon-carbon single bond, such as 1.522(2) Å in ethane.¹⁹ The C1–C2 bond length in **2** is also the same length (within three esd values) as those in $[\{(\text{calix-pyrrole})\text{Ln}\}(\mu\text{:}\eta^2\text{:}\eta^2\text{-C}_2\text{H}_4)]$.⁸ It is noteworthy that η^2 -ethene complexes, especially of late transition

metals, with long C–C distances of approximately 1.49 Å are often described as metallocyclopropanes,²⁰ suggesting that the U₂C₂ core of **2** can be regarded as a dimetalla-bicyclobutane.

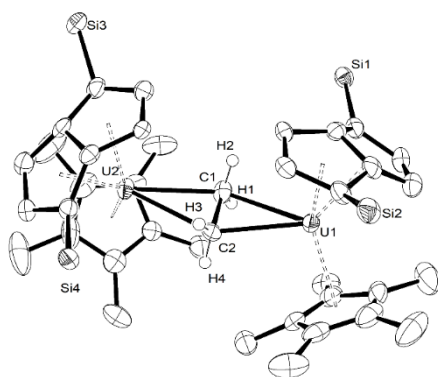
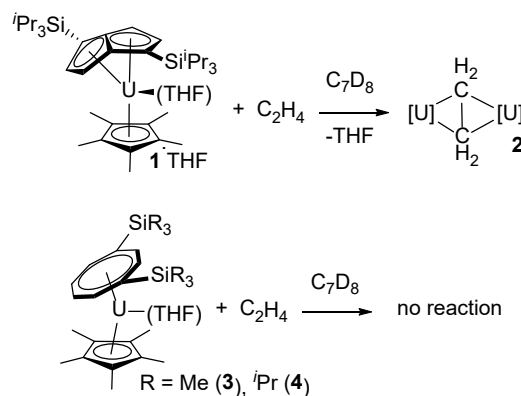


Figure 1. ORTEP diagram of the molecular structure of **2** displaying 50% anisotropic thermal parameters. *i*Pr groups and H atoms (except those on the C₂H₄ ligand) have been omitted for clarity. The hydrogen atoms on the C₂H₄ ligand were found in the difference map and refined freely.

The U–C distances within the three-membered rings of **2** differ significantly, with the U1–C1 distance of 2.534(4) Å being in the range of 2.42–2.57 Å observed for uranium(IV) benzyl complexes^{21–25} and other U–C single σ -bonds,²⁶ while the longer U1–C2 distance of 2.707(4) Å is similar to the long U–C single σ bonds found in highly strained U(IV) metallocycles.²⁷ This notion is further reflected in the C1–U1–C2 angle of 32.9(18)°.

The ¹H NMR spectrum obtained when isolated **2** is re-dissolved in toluene-*d*₈ shows the presence of small amounts of complex **1**, free ethene and complex **2**. Integration of the two Cp* resonances reveals that **1** and, therefore, ethene account for approximately 7% of the equilibrium (Figures S8 and S5). Low-temperature ¹H NMR spectroscopy reveals that, below 10°C, only **2** is present in solution. In contrast, above 70°C, **2** completely dissociates into **1** and ethene. Furthermore, **2** does not re-form upon cooling to room temperature, however adding C₂H₄ to this sample does re-form **2**. The existence of this equilibrium was further confirmed by the exchange of ethene in **2** by ¹³C₂H₄ (and *vice-versa*), although in this case an excess of ¹³C₂H₄ (at least two equivalents) was required to observe the ¹³C NMR signal in **2**-¹³C. The *K*_{eq} at 30°C was measured to be 9.2 × 10^{−8} mmol².mL^{−2} and a Van't-Hoff analysis in the temperature range between 20–40°C at 5°C intervals yielded $\Delta H = 167.5$ kJ mol^{−1} and $\Delta S = 417$ J mol^{−1} K^{−1}, implying that entropy plays a significant role in driving the dissociation of ethene.

To investigate the importance of having a base-free uranium starting material, we explored the reactivity of **1**·THF with C₂H₄ since, unlike **1**, the solvated analogue does not react with N₂. We found that **1**·THF does indeed react with C₂H₄ and ¹³C₂H₄ to produce **2**, as shown by ¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR spectroscopy (Scheme 2). Nevertheless, the reaction was not as clean, with ¹H NMR spectroscopy indicating a 70% conversion, leading to an isolated yield of 20% instead of 43% when using **1**.



Scheme 2. Contrasting reactivity of uranium(III) pentalene and cyclooctatetraene complexes with ethene.

The folded nature of η^8 -pentalene ligands has been shown to play an important role in small-molecule activation reactions mediated by uranium(III), and in many cases the same reactivity is not observed with related η^8 -cyclooctatetraene (COT) derivatives.^{15,16} When three or more equivalents of C₂H₄ were added to the uranium(III)-COT complexes [U{ η^8 -C₈H₆(1,4-SiR₃)₂}(η^8 -Cp*)(THF)] (R = Me **3**, *i*Pr **4**, Scheme 2) no reaction occurred. This observation can be explained in terms of previously reported electrochemical studies on pentalene- and COT-ligated uranium(III) complexes, with the former being more reducing in nature by 200 mV,²⁸ which further highlights the importance of the Pn⁺⁺ ligand in the activation of ethene.

The formation of **2** and the uranium-ethene bonding were investigated by density functional theory (DFT) at the B3PW91 level. The formation of **2** was computed to be thermodynamically favored by 22.9 kcal mol^{−1}, which is very similar to the stabilization found in the case of the coordination of CO₂ prior to its reductive transformation by uranium(III) complexes.²⁹ Analysis of the bonding reveals that the highest-occupied molecular orbital (HOMO) involves the ethene π^* orbital and hybrid 6*d*–5*f* orbitals on uranium (Figures 2 and S24).

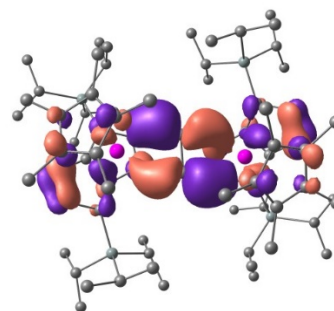


Figure 2. Molecular orbital corresponding to the uranium-ethene bonding in **2**.

The nature of this interaction was further elucidated using Natural Bonding Orbital (NBO) analysis. Two U–C natural localized MOs (NLMOs) were obtained and, in both cases, are strongly polarized toward carbon, which provides an 88.8% contribution; this result implies a formal double reduction of ethene by uranium. The uranium centers are involved in the bonding through a hybrid 6*d*–5*f* orbital, with contributions of 85.4% and 14.6%, respectively. The system is therefore best described as a di-uranium dialkyl complex, which is equivalent to the dimetalla-bicyclobutane U₂C₂

core proposed on the basis of the experimental structure data. Indeed, the Wiberg bond indices (WBIs) are 0.36 for the U–C interactions, suggesting that the bond is predominantly ionic in character but with a small-but-significant covalent contribution, as often found in uranium organometallics.³⁰

The crystallographic and computational results on **2** suggest that coordination of ethene results in formal oxidation of the two U(III) centres to U(IV). To provide support for this notion, the temperature-dependence of the magnetic susceptibility of **2** was studied in an applied magnetic field of 0.1 T in the temperature range 2–300 K. The $\chi_M T(T)$ plot (where χ_M is the molar magnetic susceptibility, Figures 3, S22, S23) shows characteristic behaviour for two non-interacting U(IV) centres, with a $\chi_M T$ value that approaches zero at 0 K, consistent with a non-magnetic 3H_4 ground state.³¹ The absence of a maximum in the $\chi_M^{-1}(T)$ (Figure 3) also suggests that the two uranium(IV) centres are not exchange-coupled to any appreciable extent.

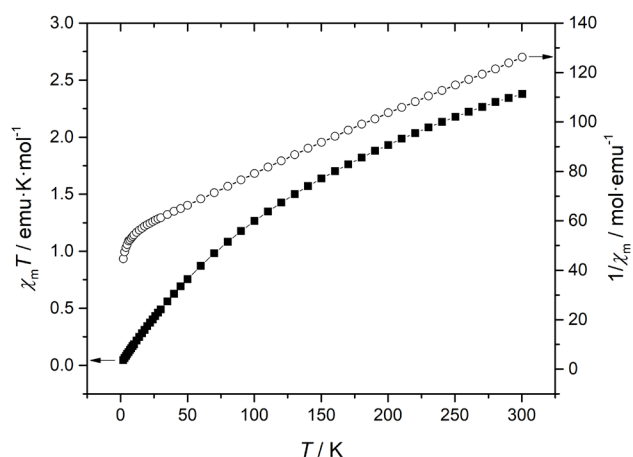
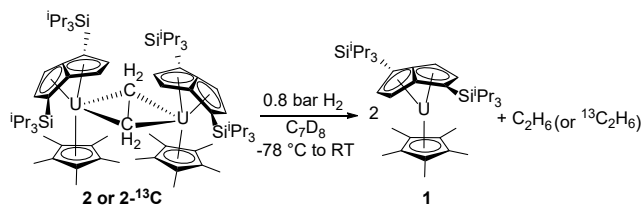


Figure 3. Molar magnetic susceptibility data for **2** in an applied field of 0.1 T, showing $\chi_M T$ (black squares) and χ_M^{-1} (hollow circles) as functions of temperature.

The extent to which the ethene double bond has been disrupted in **2** relative to free ethene prompted us to investigate the reactivity of the complex with dihydrogen. Indeed, complex **2** reacts readily with H_2 at room temperature at atmospheric pressure to produce ethane and regenerate complex **1** in solution (Scheme 3, Figures S17–S20). In light of this observation, we decided to investigate whether **1** could catalyze the hydrogenation of C_2H_4 . With loadings as low as 0.5 mol % of **1**, full conversion of C_2H_4 to C_2H_6 is observed within 90 minutes at room temperature. To the best of our knowledge, the catalytic hydrogenation of an alkene by a uranium catalyst has not previously been observed. Furthermore, during catalysis, the formation of complex **2** was observed by 1H NMR spectroscopy (Figure S23). The detailed mechanism of the hydrogenation catalysis will form part of our on-going work.



Scheme 3. Reactivity of **2** towards hydrogen.

In conclusion, the uranium(III) centre in the pentalene complex **1** allows coordination and activation of ethene, resulting in the formation of the uranium(IV) dimetalla-bicyclobutane complex **2**. The uranium-carbon bonding to the activated C_2H_4 ligand in **2** is characterized by a δ -type interaction with appreciable contributions from the uranium $5f$ and $6d$ orbitals. The discovery of **2** and its reaction with hydrogen under mild conditions to form ethane and regenerate **1** introduces potential for the uranium-based activation of alkenes to be extended to higher alkenes and other unsaturated organic compounds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Synthesis, spectroscopic characterization, crystallography details, theoretical calculations (PDF).

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Notes

The authors declare no competing financial interests.

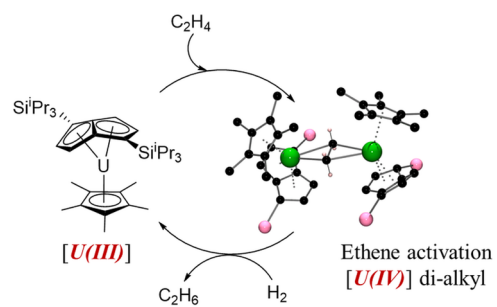
ACKNOWLEDGMENT

This paper is dedicated to Dick Andersen. We would like to thank the EPSRC (EP/M023885/1) and the ERC (CoG grant RadMag, 646740), as well as Dr Nickolas Rees (University of Oxford) for access to solid state NMR facilities.

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